

Soft segment free thermoplastic polyester elastomers with high performance†

Fei Liu,^a Junwu Zhang,^a Jinggang Wang,^a Xiaoqing Liu,^a Ruoyu Zhang,^a Guohua Hu,^b Haining Na^{*a} and Jin Zhu^{*a}

A soft segment free thermoplastic polyester elastomer is fabricated by controlling the stereochemical structure of molecular chains with the utilization of the *cis* 1,4-cyclohexylene ring moiety (*cis*-CHRM) in poly(butylene 1,4-cyclohexanedicarboxylate) (PBC). PBC with 71% *cis*-CHRM exhibits good elasticity with shape recovery rates of 64% at 200% strain and 92% at break, tensile modulus, strength and elongation at break at 111 and 18 MPa and 1230%, respectively.

Introduction

Thermoplastic elastomers (TPEs) are a particular class of polymeric materials that possess both the facile processability of plastic and the superior elasticity of rubber.¹ Over the past few decades, the traditional strategy to synthesize TPEs has been to introduce amorphous and flexible soft segments into thermoplastic polymer chains. Soft segments form micro-phase separated structures in the TPE matrix, providing superior elasticity. This traditional strategy has allowed for the development of many types of TPEs such as styrenic thermoplastic elastomers (TPSS),² thermoplastic polyurethane elastomers (TPUs),^{3,4} thermoplastic poly(ether-amide) elastomers (TPAEs)⁵ and thermoplastic poly(ether-ester) elastomers (TPEEs).^{6,7}

However, it is not ideal to introduce soft segments into a thermoplastic polymer chain because it always inevitably brings about a decrease in thermal and tensile properties of the thermoplastic polymer.⁸ Therefore, it is interesting to develop an alternative methodology to synthesize TPEs without sacrificing their overall properties. As mentioned above, it is crucial not to

introduce soft segments into TPEs in order to maintain their good tensile and thermal properties. On the other hand, the use of soft segments to induce “soft” phases in the TPE matrix is a prerequisite to initiate superior elasticity. Thus the traditional strategy is not suitable for fabricating TPEs with high overall tensile and thermal properties. It is therefore necessary to develop an alternative way to gain elasticity without using soft segments. It is well known that flexible polymer chains such as rubber and elastomers possess entropic elasticity and are able to recover their original shape after large deformation. This property is exactly like the one exhibited by soft segments in traditional TPEs. The only important difference between a plastic and a traditional TPE lies in the “soft” phases. This difference essentially suggests that a polymer with flexible chains can exhibit intrinsic elasticity if interactions between flexible chains are small. This inspires us to create a novel strategy to synthesize soft segment free TPEs by releasing the intrinsic elasticity of polymer chains. Accordingly, high performance particularly high mechanical and thermal properties can be expected.

The most effective way to reduce intra-limitations between polymer chains is to introduce an irregular structure. For example, polybutadiene (PB) can be either a plastic or a rubber, depending on its stereochemical structure. 1,3-Butadiene can be polymerized to PB mainly in two ways, 1,4-*trans* and 1,4-*cis*.^{9,10} PB with a large number of 1,4-*trans* butadiene moieties can easily crystallize because of its regular structure, resulting in strong interactions between polymer chains. On the other hand, PB with a large number of irregular 1,4-*cis* butadiene moieties does not crystallize. The amorphous phases show the properties of a synthetic rubber. The aim of this work is to simultaneously improve the rigidity and toughness of polymers by incorporating non-planar hexatomic rings into their chains. Hexatomic rings are relatively rigid and at the same time are able to exhibit two different stereochemical structures (*cis* and *trans*, which are irregular and regular, respectively) in the synthesis of polymers.¹¹⁻¹³ Accordingly, new TPEs containing non-planar hexatomic rings are expected.

^aNingbo Key Laboratory of Polymer Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo, Zhejiang 315201, P. R. China. E-mail: jzhu@nimte.ac.cn; nahaining@nimte.ac.cn

^bLaboratory of Reactions and Process Engineering, Université de Lorraine-CNRS, 1 rue Grandville, BP 20451, 54001 Nancy, France

The literature reported on the use of the 1,4-cyclohexylene ring moiety (CHRM), especially the *trans*-CHRM in the synthesis of thermoplastic polymers (particularly polyesters).^{13–19} As for poly(butylene 1,4-cyclohexanedicarboxylate) (PBC), the *cis*-CHRM is rarely used.^{20–29} Therefore, only the properties of PBC as a plastic are studied.^{24–27} The effect of the *cis*-CHRM on its elasticity has been ignored. In this communication, we discuss on the effect of the *cis*-CHRM on the properties of PBC for the first time. By tuning the stereochemical structure of the CHRM, a new soft segment free TPE with high overall mechanical properties is proposed. Accordingly, a simple and effective strategy to synthesize soft segment free TPEs with high performance is established.

Experimental section

Synthesis

PBC was synthesized *via* a conventional melt polycondensation process from CHDA and BDO using titanium(IV) butoxide as a catalyst (Scheme 1).¹³ The PBC samples are denoted as PBC_x, where *x* is the number of *cis*-CHRM in the polymer chain.

Characterization

Molecular weights and molecular weight distributions were measured on a PL-GPC220 gel permeation chromatograph (GPC). The structure and the number of *cis*-CHRM in the polymer chains of PBC were determined by proton nuclear magnetic resonance (¹H NMR) in CDCl₃ solvent using a Bruker AVIII400 NMR spectrometer at room temperature. Differential scanning calorimetry (DSC) measurements were performed using a differential scanning calorimeter of type METTLER-TOLEDO DSC I. Thermal stability measurements were conducted using a Mettler-Toledo TGA/DSC thermogravimetric analyzer (TGA). Dynamic mechanical analysis (DMA) was conducted with a METTLER-TOLEDO dynamic mechanical analyzer (DMA/SDTA861e) at a fixed frequency of 1 Hz, operating in the film tension mode. Tensile testing and cyclic tensile

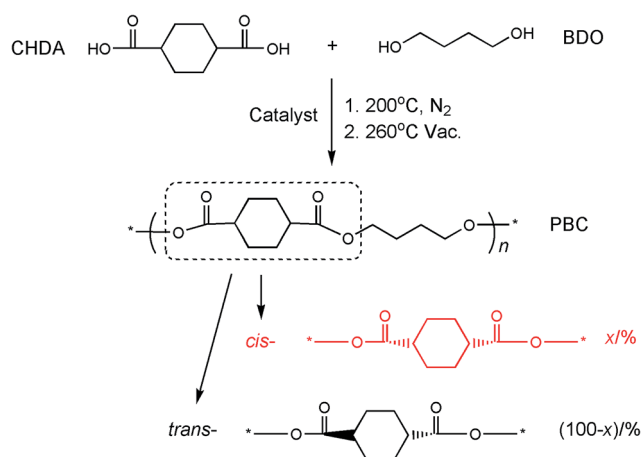
testing were performed using an Instron5567 tensile testing machine with a load cell of 500 N.

Detailed information about synthesis and characterization is provided in the ESI.†

Results and discussion

PBCs are synthesized *via* a convenient melt polycondensation process from 1,4-cyclohexanedicarboxylic acid (CHDA) with 1,4-butanediol (BDO) (Scheme 1). The number of *cis*-CHRM in the final products ranges from 12 to 71% (Table 1), as determined by ¹H NMR (Fig. 1). Deviation of the final compositions from the feed ones is observed due to the isomerization between *cis* and *trans* isomers at high temperature.³⁰ In fact, the number of *cis*-CHRM at thermodynamic equilibrium is 34%,¹⁷ and once it is not in this balanced state at high temperature, isomerization is inevitable. The more the deviation from the balanced state, the more isomerization will occur. Thus only 1% and 6% of isomerization are found for PBC36 and PBC44, respectively, but 11% and 26% of isomerization occurred for PBC12 and PBC71, respectively. All samples have a similar number-average molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) of about 30 000 and 2.5, respectively (Table 1). Thus differences in the properties of PBC mainly depend on the number of *cis*-CHRM.

PBC turns from a semicrystalline polymer to an amorphous one when the number of *cis*-CHRM increases from 12 to 71% (Table 2). An interesting phenomenon is observed for PBC44, whose second heating scan shows cold crystallization and melting temperature (*T_m*) (Fig. 2a), while the cooling scan does not show a crystallization temperature (*T_c*) (Fig. 2b). This phenomenon indicates that when the number of *cis*-CHRM increases from 12% to 44%, the irregular structure introduces more “kinks” into the polymer chain,¹³ which will hinder the formation of crystalline domains by *trans*-CHRM when cooling from melt. However, a substantial number of *trans*-CHRM in the polymer chain (56% for PBC44) can still induce cold crystallization when the polymer chain is flexible at a temperature higher than the glass transition temperature. Thus the second heating scan of PBC44 shows cold crystallization and *T_m*. Given



Scheme 1 Synthesis of PBC from CHDA and BDO.

Table 1 Composition and molecular weight of PBC

| Sample | <i>cis</i> -CHRM% | | <i>M_n</i> ^c | <i>M_w</i> / <i>M_n</i> ^c |
|--------|-------------------|--------------------|-----------------------------------|--|
| | Feed ^a | Final ^b | | |
| PBC12 | 1 | 12 | 33 000 | 2.5 |
| PBC36 | 37 | 36 | 30 000 | 2.1 |
| PBC44 | 50 | 44 | 30 000 | 2.2 |
| PBC71 | 97 | 71 | 30 000 | 2.5 |

^a 99% *trans*-CHDA, *mix*-CHDA (*cis/trans* 50/50) and 97% *cis*-CHDA were used as starting materials for PBC12, PBC44 and PBC71, respectively, and a mixture of 99% *trans*-CHDA and *mix*-CHDA was used as a starting material for PBC36. ^b Calculated from ¹H NMR in CDCl₃ based on the integration of signals at 2.47 ppm and 2.28 ppm, which could be assigned to the protons of -CH- in *cis*- and *trans*-CHRM, respectively. ^c Determined by GPC in CHCl₃.

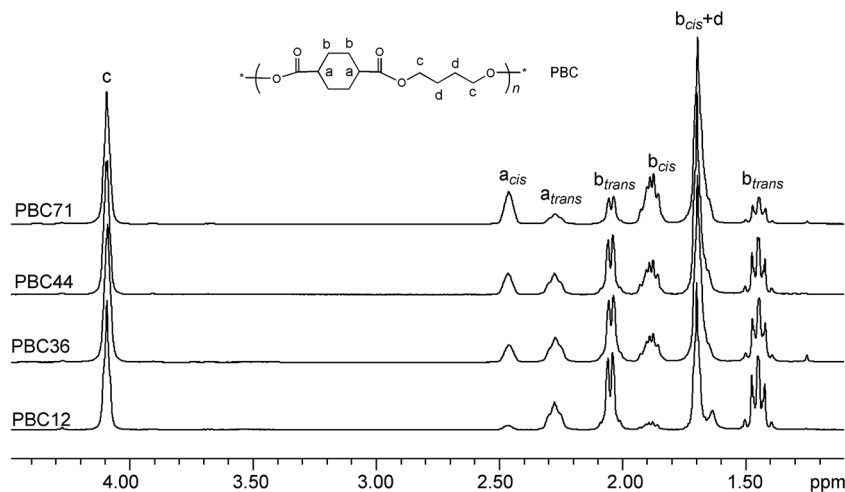


Fig. 1 ^1H NMR spectra (CDCl_3 , 400 MHz) of PBC.

Table 2 Thermal properties of PBC

| Sample | T_m^a [$^{\circ}\text{C}$] | T_c^a [$^{\circ}\text{C}$] | χ_c^a [%] | T_g^a [$^{\circ}\text{C}$] | T_{α}^b [$^{\circ}\text{C}$] | $T_{5\%}^c$ [$^{\circ}\text{C}$] | |
|--------|--------------------------------|--------------------------------|----------------|--------------------------------|---------------------------------------|------------------------------------|-----|
| | | | | | | N_2 | Air |
| PBC12 | 147 | 125 | 19.4 | 5.0 | 27.5 | 382 | 370 |
| PBC36 | 102 | 66 | 18.7 | -4.0 | 7.5 | 380 | 363 |
| PBC44 | 89 | — | 10.7 | -4.5 | 7.5 | 380 | 363 |
| PBC71 | — | — | 0.0 | -8.0 | 5.0 | 378 | 365 |

^a Determined by DSC, T_m , melting temperature, T_c , crystallization temperature, χ_c , degree of crystallinity and T_g , glass transition temperature. ^b Determined by DMA (Fig. S1 and S2), T_{α} , α transition temperature. ^c Determined by TGA, $T_{5\%}$, temperature at which the weight loss is 5%.

that both PBC12 and PBC36 have T_m and T_c , while PBC71 has no T_m , the transition of PBC from a semicrystalline polymer to an amorphous one should occur between 36% and 44%. Berti *et al.* found a value close to this range.¹³ Moreover, an increase in the number of *cis*-CHRM results in a steady decrease in the glass transition temperature, as evidenced by both DSC (T_g) and DMA (T_{α}) (Table 2). Therefore, the incorporation of *cis*-CHRM plays a role in reducing the interactions among PBC chains and therefore their ability to crystallize.^{13,31} In addition, all PBCs have high thermal stability regardless of the number of *cis*-CHRM (Table 2), with $T_{5\%}$ around 380 $^{\circ}\text{C}$ in N_2 and 365 $^{\circ}\text{C}$ in air atmosphere, respectively.

The fact that PBC changes from a semicrystalline polymer to an amorphous one as the number of *cis*-CHRM increases has a significant effect on its tensile properties. Table 3 shows the tensile properties of PBC with different numbers of *cis*-CHRM and Fig. 3 shows the representative strain–stress curves. It is seen that all four samples show strain–stress curves for a typical thermoplastic polyester which consists of four regions:³² (1) linear and non-linear viscoelasticity, (2) neck region/strain softening, (3) plastic flow and (4) strain hardening. For the three semicrystalline samples, as the number of *cis*-CHRM increases,

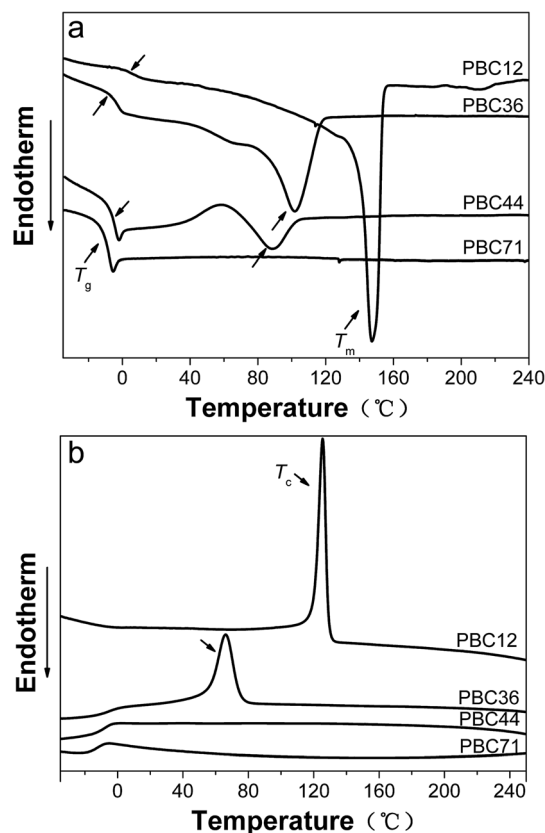


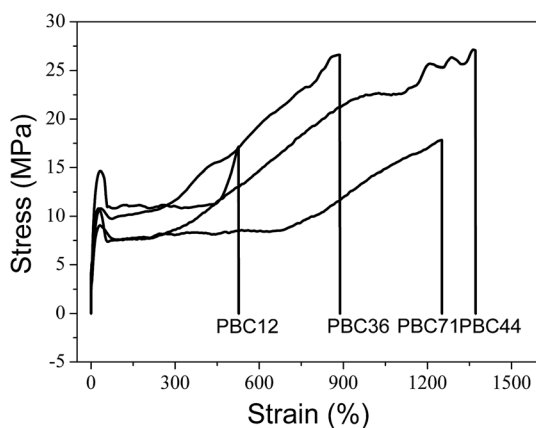
Fig. 2 DSC curves of PBC in the (a) second heating and (b) cooling scans.

χ_c decreases. Thus E and σ_y decrease whereas σ_t , ϵ_b and ϵ_y increase, as expected. On the other hand, it is interesting to note that the tensile properties especially E of PBC71 and PBC12 are comparable except ϵ_b which differs greatly. It is 1230% and 520% for PBC71 and PBC12, respectively. A higher ϵ_b is due to a larger amount of the amorphous region. A fully amorphous sample is expected to have a much higher ϵ_b than a

Table 3 Tensile properties of PBC^a

| Sample | E [MPa] | σ_t [MPa] | ε_b [%] | σ_y [MPa] | ε_y [%] |
|--------|-----------|------------------|---------------------|------------------|---------------------|
| PBC12 | 157 ± 7 | 17 ± 1 | 520 ± 7 | 14 ± 1 | 21 ± 1 |
| PBC36 | 99 ± 10 | 27 ± 1 | 880 ± 17 | 11 ± 0.4 | 26 ± 4 |
| PBC44 | 81 ± 12 | 28 ± 1 | 1360 ± 28 | 9 ± 1 | 28 ± 2 |
| PBC71 | 111 ± 12 | 18 ± 1 | 1230 ± 35 | 11 ± 0.4 | 26 ± 1 |

^a Determined by tensile testing, Young's modulus (E), tensile strength (σ_t), elongation at break (ε_b), stress at yield (σ_y), and strain at yield (ε_y).

**Fig. 3** Representative tensile strain-stress curves of PBC.**Table 4** Elastic properties of PBC^a

| Sample | $R_r(1)$ [%] | $R_r(2)$ [%] | $R_r(3)$ [%] | $R_r(4)$ [%] | $R_r(5)$ [%] | R_{rb} [%] |
|--------|--------------|--------------|--------------|--------------|--------------|--------------|
| PBC12 | 11 ± 1 | 95 ± 2 | 97 ± 1 | 100 ± 2 | 100 ± 5 | 38 |
| PBC36 | 35 ± 1 | 93 ± 3 | 96 ± 1 | 97 ± 1 | 100 ± 2 | 53 |
| PBC44 | 41 ± 2 | 91 ± 1 | 96 ± 2 | 98 ± 1 | 99 ± 1 | 68 |
| PBC71 | 64 ± 4 | 96 ± 2 | 97 ± 2 | 99 ± 1 | 100 ± 1 | 92 |

^a The recovery rate at 200% strain ($R_r(N)$) for the N th cycle in the cyclic tensile testing and the recovery rate at break (R_{rb}).

semicrystalline one. However, due to the strain hardening effect,³³ PBC44 has the highest ε_b although the amount of amorphous region of PBC44 is smaller than that of PBC71.

The elastic properties of PBC are investigated by cyclic tensile testing. Table 4 shows the recovery rates of the cyclic tensile testing with 200% strain (R_r). When the number of *cis*-CHRM increases from 12% to 71%, the first cycle recovery rate of PBC increases steadily from 11% to 64%, confirming the shift of PBC from a plastic to a TPE. The elastic properties of PBC are also shown by the shape recovery rate at break (R_{rb}) (Table 4). The R_{rb} of PBC increases as the number of *cis*-CHRM increases and reaches 92% with 71% *cis*-CHRM.

The high elasticity of traditional TPEs originates from soft segments.³⁴ It is like part of the polymer chains of a hard plastic are modified to become soft. The intrinsic entropic elasticity of hard segments is restrained due to high T_g or strong interactions between molecular chains such as crystallization and hydrogen bonding. Thus polymer chains are either frozen in a

glassy state (e.g. polystyrene and PBT) or the chain mobility is restricted by strong interactions between polymer chains (e.g. polyamide and polyurethane). As a result, soft segments have to be incorporated by copolymerization or blending to introduce external entropic elasticity. In fact, it is impossible for this type of modification to completely avoid the obvious decrease of mechanical modulus and strength.

By contrast, the strategy we have developed is to modify polymer chains in such a way that their intrinsic entropic elasticity can be fully released. The formation of an amorphous region by the incorporation of irregular non-planar ring moieties into polymer chains promotes the effective release of the intrinsic entropic elasticity of PBC. Since PBC with a full *trans*-CHRM is a semicrystalline plastic with a T_g of 18 °C,¹³ part of the polymer chains are flexible and in their rubber-elastic state at room temperature but are restricted by the crystalline domains. Thus breaking the crystalline domains formed by *trans*-CHRM will release the intrinsic entropic elasticity and achieve the transition from a plastic to a TPE. Manipulation of stereochemistry, i.e., partial replacement of a *trans*-CHRM by a *cis*-CHRM whose structure is irregular, successfully results in the shift of PBC from a plastic to a TPE. The *cis*-CHRM not only plays a role as an irregular structure to break the crystalline domains but also decreases the T_g of PBC. It is noteworthy that TPEs with intrinsic entropic elasticity are flexible amorphous materials. Instead of calling upon crystallization or strong interactions, they have chain entanglements which act as physical net points to prevent excessive chain slipping which would result in permanent deformation.^{34,35} In the case of PBC, chain entanglements not only prevent large permanent deformation upon an external stress (the permanent deformation at break of PBC with 71% *cis*-CHRM is only 8%), but also are responsible for the high E , which is even comparable to that of the semicrystalline PBC. Similar processes with the aim to alter the regularity of polymer chains are the copolymerization of ethylene with vinyl acetate and to produce ethylene-vinyl acetate elastomers (EVAs) and that of propylene (or a third diene monomer (DM)) to produce ethylene-propylene elastomers (EP or EPDMs).

Another advantage of using non-planar ring moieties to synthesize TPEs is that it is possible to obtain both superior elasticity and high mechanical modulus and strength. Table 3 shows that E , σ_t and ε_b of PBC71 are as high as 111 MPa, 18 MPa and 1230%, respectively. Their modulus and strength are much higher than those of a TPE obtained by the traditional strategy.^{8,36–40}

Conclusions

In summary, we have developed a soft segment free strategy for the synthesis of high performance TPEs *via* the manipulation of stereochemistry for plastics with intrinsic entropic elasticity. By incorporation of irregular non-planar ring moieties into polymer chains, the crystalline region is disrupted and the intrinsic entropic elasticity is released. Compared with TPEs obtained by the traditional strategy, the new strategy reported in this paper with the manipulation of stereochemistry of CHRM is much

simpler and more effective to achieve soft segment free TPES with high overall mechanical and thermal properties. More importantly, our research provides a new guideline for the synthesis of TPES from plastics based on the release of the intrinsic entropic elasticity from their polymer chains.

Acknowledgements

The authors are grateful for the financial support by the Key Research Program of the Chinese Academy of Sciences (KGZD-EW-606-16), Ningbo Natural Science Foundation (no. 2013A610025 and no. 2013A610023), and Ningbo Key Lab of Polymer Materials (Grant no. 2010A22001).

Notes and references

- 1 R. J. Spontak and N. P. Pate, *Curr. Opin. Colloid Interface Sci.*, 2000, **5**, 334.
- 2 H. Schmalz, A. Bo, R. Lange and G. Krausch, *Macromolecules*, 2001, **34**, 8720.
- 3 L. Zhang, Y. Jiang, Z. Xiong, X. Liu, H. Na, R. Zhang and J. Zhu, *J. Mater. Chem. A*, 2013, **1**, 3263.
- 4 R. Yu, L. Zhang, Y. Feng, R. Zhang and J. Zhu, *Chin. J. Polym. Sci.*, 2014, **32**, 1099.
- 5 N. J. Sijbrandi, A. J. Kimenai, E. P. C. Mes, R. Broos, G. Bar, M. Rosenthal, Y. Odarchenko, D. A. Ivanov, P. J. Dijkstra and J. Feijen, *Macromolecules*, 2012, **45**, 3948.
- 6 J. G. Drobný, *Handbook of Thermoplastic Elastomers*, William Andrew Publishing, 2007, p. 249.
- 7 G. K. Hoeschele, *Polym. Eng. Sci.*, 1974, **14**, 848.
- 8 A. A. Deschamps, D. W. Grijpma and J. Feijen, *Polymer*, 2001, **42**, 9335.
- 9 Y. Li and W. L. Mattice, *Macromolecules*, 1992, **25**, 4942.
- 10 N. M. T. Pires, F. M. B. Coutinho and M. S. Costa, *Eur. Polym. J.*, 2004, **40**, 2599.
- 11 L. P. Chen, A. F. Yee, J. M. Goetz and J. Schaefer, *Macromolecules*, 1998, **31**, 5371.
- 12 J. Liu and A. F. Yee, *Macromolecules*, 1998, **31**, 7865.
- 13 C. Berti, A. Celli, P. Marchese, E. Marianucci, G. Barbiroli and F. Di Credico, *Macromol. Chem. Phys.*, 2008, **209**, 1333.
- 14 C. Berti, A. Celli, P. Marchese, E. Marianucci, S. Sullalti and G. Barbiroli, *Macromol. Chem. Phys.*, 2010, **211**, 1559.
- 15 A. Celli, P. Marchese, S. Sullalti, C. Berti and G. Barbiroli, *Macromol. Chem. Phys.*, 2011, **212**, 1524.
- 16 B. Vanhaecht, B. Rimez, R. Willem, M. Biesemans and C. E. Koning, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1962.
- 17 H. R. Kricheldorf and G. Schwarz, *Makromol. Chem.*, 1987, **188**, 1281.
- 18 C. Berti, E. Binassi, A. Celli, M. Colonna, M. Fiorini, P. Marchese, E. Marianucci, M. Gazzano, F. D. I. Credico and D. J. Brunelle, *J. Polym. Sci., Part B: Polym. Phys.*, 2008, **46**, 619.
- 19 M. Colonna, C. Berti, E. Binassi, A. Celli, M. Fiorini, P. Marchese, M. Messori and D. J. Brunelle, *Polym. Int.*, 2011, **60**, 1607.
- 20 B. Davis and F. D. Petke, *US Pat.*, 4,075,180, 1978.
- 21 W. J. Jackson, *US Pat.*, 4,327,206, 1982.
- 22 W. Borman, *US Pat.*, 5,399,661, 1995.
- 23 D. J. Brunelle, *US Pat.*, 6,084,055, 2000.
- 24 D. J. Brunelle and T. Jang, *Polymer*, 2006, **47**, 4094.
- 25 M. Gigli, N. Lotti, M. Vercellino, L. Visai and A. Munari, *Mater. Sci. Eng., C*, 2014, **34**, 86.
- 26 M. Gigli, N. Lotti, M. Gazzano, V. Siracusa, L. Finelli, A. Munari and M. D. Rosa, *Polym. Degrad. Stab.*, 2014, **105**, 96.
- 27 M. Gigli, N. Lotti, M. Gazzano, V. Siracusa, L. Finelli, A. Munari, M. D. Rosa, I. Industriale, U. Catania and V. A. Doria, *Ind. Eng. Chem. Res.*, 2013, **52**, 12876.
- 28 L. Wang, Z. Xie, X. Bi, X. Wang, A. Zhang, Z. Chen, J. Zhou and Z. Feng, *Polym. Degrad. Stab.*, 2006, **91**, 2220.
- 29 T. E. Sandhya, C. Ramesh and S. Sivaram, *Macromolecules*, 2007, **40**, 6906.
- 30 B. Vanhaecht, M. N. Teerenstra, D. R. Suwier, R. Willem, M. Biesemans and C. E. Koning, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 833.
- 31 M. A. Osman, *Macromolecules*, 1986, **19**, 1824.
- 32 J. A. Mason and R. W. Hertzberg, *CRC Crit. Rev. Macromol. Sci.*, 1973, **1**, 433.
- 33 R. Gohil, *Polym. Eng. Sci.*, 2009, **49**, 544.
- 34 A. Lendlein and S. Kelch, *Angew. Chem., Int. Ed.*, 2002, **41**, 2034.
- 35 Q. Liu, L. Jiang, R. Shi and L. Zhang, *Prog. Polym. Sci.*, 2012, **37**, 715.
- 36 G. K. Hoeschele, *Polym. Eng. Sci.*, 1974, **14**, 848.
- 37 E. V. Konyukhova, V. M. Neverov, Y. K. Godovsky, S. N. Chvalun and M. Soliman, *Macromol. Mater. Eng.*, 2002, **287**, 250.
- 38 A. Szymczyk, E. Senderek, J. Nastalczyk and Z. Roslaniec, *Eur. Polym. J.*, 2008, **44**, 436.
- 39 Y. Zhang, Z. Feng and A. Zhang, *Polym. Int.*, 2003, **52**, 1351.
- 40 J. Zhang, F. Liu, J. Wang, H. Na and J. Zhu, *Chin. J. Polym. Sci.*, 2015, DOI: 10.1007/s10118-015-1673-4.